

Copper-Containing Ceramic Precursor Synthesis: Solid-State Transformations and Materials Technology

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COPPER-CONTAINING CERAMIC PRECURSOR SYNTHESIS: SOLID-STATE TRANSFORMATIONS AND MATERIALS TECHNOLOGY

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ABSTRACT

Three copper systems with relevance to materials technology are discussed. In the first, a CuS precursor, $\text{Cu}_4\text{S}_{10}(\text{4-methylpyridine})_4$ (4-MePy), was prepared by three routes: reaction of Cu_2S , reaction of $\text{CuBr}\cdot\text{SMe}_2$ and oxidation of copper powder with excess sulfur in 4-methylpyridine by sulfur. In the second, copper powder was found to react with excess thiourea ($\text{H}_2\text{NC(S)NH}_2$) in 4-methylpyridine to produce thiocyanate (NCS^-) complexes. Three isolated and characterized compounds are: $\text{Cu}(\text{NCS})(\text{4-MePy})_2$, a polymer, $[\text{4-MePy}\cdot\text{H}][\text{Cu}(\text{NCS})_3(\text{4-MePy})_2]$, a salt, and $\text{t-Cu}(\text{NCS})_2(\text{4-MePy})_4$. Finally, an attempt to produce a mixed-metal sulfide precursor of Cu and Ga in N-methylimidazole (N-MeIm) resulted in the synthesis of a Cu-containing polymer, $\text{Cu}(\text{SO}_4)(\text{N-MeIm})$. The structures are presented; the chemistry will be briefly discussed in the context of preparation and processing of copper-containing materials for aerospace applications.

INTRODUCTION

The chemical and physical properties of copper have resulted in its use going back to ancient times [1]. Current technological applications include thin-films of the metal in electronics [2], use of sulfides and mixed-metal chalcogenides in photovoltaics [3], and as a component of the recently-discovered high-temperature ceramic superconductors [4]. All three of these technologies offer research opportunities for chemists and materials scientists involved in materials fabrication and processing.

Due to the critical importance of copper as an interconnect metal in microelectronics, there has been an international effort to produce selective chemical vapor deposition (CVD) precursors [5-8]. Also, the lack of a simple, effective dry etch for copper has resulted in a large effort to understand mechanisms for copper etching in heterogeneous systems [9-12]. Other areas of active chemical research relevant to copper include: the search for precursors for copper-containing materials such as CuInQ_2 ($\text{Q} = \text{S}$ or Se) [13,14] for thin-film photovoltaics; rare-earth, bismuth, and thallium ceramic superconductors, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_8$, and $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ and related metal-doped compounds for numerous applications [15,16]; and the synthesis of catalysts for the chemical and petroleum industries [17]. In our efforts to prepare new copper-containing precursors for aerospace applications, we have discovered a number of new compounds and new chemistry. We highlight selected reaction chemistry and the relevant structures.

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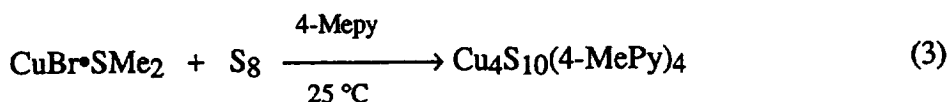
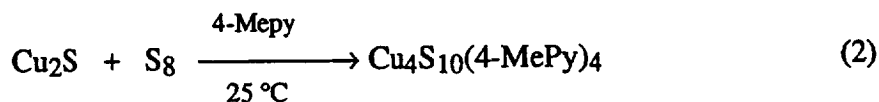
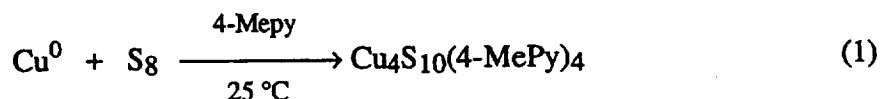
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EXPERIMENTAL

All operations of moisture- and air-sensitive materials were performed under an inert atmosphere using standard Schlenk techniques and a double-manifold vacuum line. Solids were manipulated in a Vacuum Atmospheres Co. drybox equipped with an HE-493 dri-train. Copper, thiourea ($\text{H}_2\text{NC}(\text{S})\text{NH}_2$) and sulfur (Aldrich), and $\text{CuBr}\cdot\text{SMe}_2$ (Alfa) were used without additional purification. The synthesis of $[\text{((CH}_3)_3\text{C)}_2\text{Ga}(\mu\text{-SH})]_2$ is described in [18]. The instrumental details are given in [18].

RESULTS AND DISCUSSION

In 1990, Rauchfuss et. al. reported that the reaction of Cu with S_8 in pyridine ($\text{C}_5\text{H}_5\text{N}$, Py), (1), produces the cluster $\text{Cu}_4\text{S}_{10}(\text{Py})_4\cdot\text{Py}$, where Py is a solvent of crystallization in the solid-state structure [20]. We report here that carrying out the reaction in 4-methylpyridine produces the cluster $\text{Cu}_4\text{S}_{10}(\text{4-methylpyridine})_4\cdot\text{4-methylpyridine}$ (4-MePy) (1) whose Cu_4S_{10} cluster unit is the same as that of the Rauchfuss compound. The 4-methylpyridine cluster (1) can also be prepared by other routes. In fact, compound (1) was first produced by the reaction of Cu_2S with excess sulfur in 4-methylpyridine as shown in equation (2). It has also been prepared according to equation (3) in which $\text{CuBr}\cdot\text{SMe}_2$ reacts with S_8 . The structure of compound (1) was determined by x-ray crystallography. The structure determination shows that this compound consists of two pentasulfide chains linking four Cu(I) ions each with a coordinating 4-methylpyridine and has approximate S_4 symmetry. The structure of (1) is shown in figure 1. Selected structural parameters are given in table 1.



Computer enhancement of a featureless electronic absorption spectrum yielded a single peak in the near ultraviolet ($\lambda = 334\text{ nm}$, $\epsilon = 10,000$), most likely an intraligand transition [21]. Cyclic voltammetry indicates that (1) undergoes an irreversible oxidation and reduction at -0.25 and -0.58 V vs. SCE, respectively, at 298 K in 4-methylpyridine when swept at 20 mV/sec . It is logical to conclude that oxidation takes place at the copper atoms, destabilizing tetrahedral geometry, leading to decomposition. Reduction is most likely to occur at the polysulfide ligands, leading to the decomposition of the cluster through the production of smaller S_x^{2-} units.

The compound seems to form quite readily in systems of Cu(I)-polysulfide chemistry. Similar reaction conditions with other metals did not produce analogs of (1), but instead produced $[\text{M}(\text{N-MeIm})_6]\text{S}_8$ for $\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{and Ni}$, (N-MeIm) = N-methylimidazole ($\text{N}(\text{CH}_3)\text{NC}_3\text{H}_3$) [22]. However, Cu_2S also served as a starting material for the production of the N-MeIm analog of (1), (2) [22]. The pyridine analog of compound (1) was found to produce CuS quite readily at $200\text{ }^\circ\text{C}$ by Rauchfuss et al. [20]. Its facile formation but ease of decomposition seems to be a result of the metastability of Cu(I); even moderate temperatures, by solid-state processing standards drives the redox chemistry of Cu^+ and S_x^{2-} to form CuS.

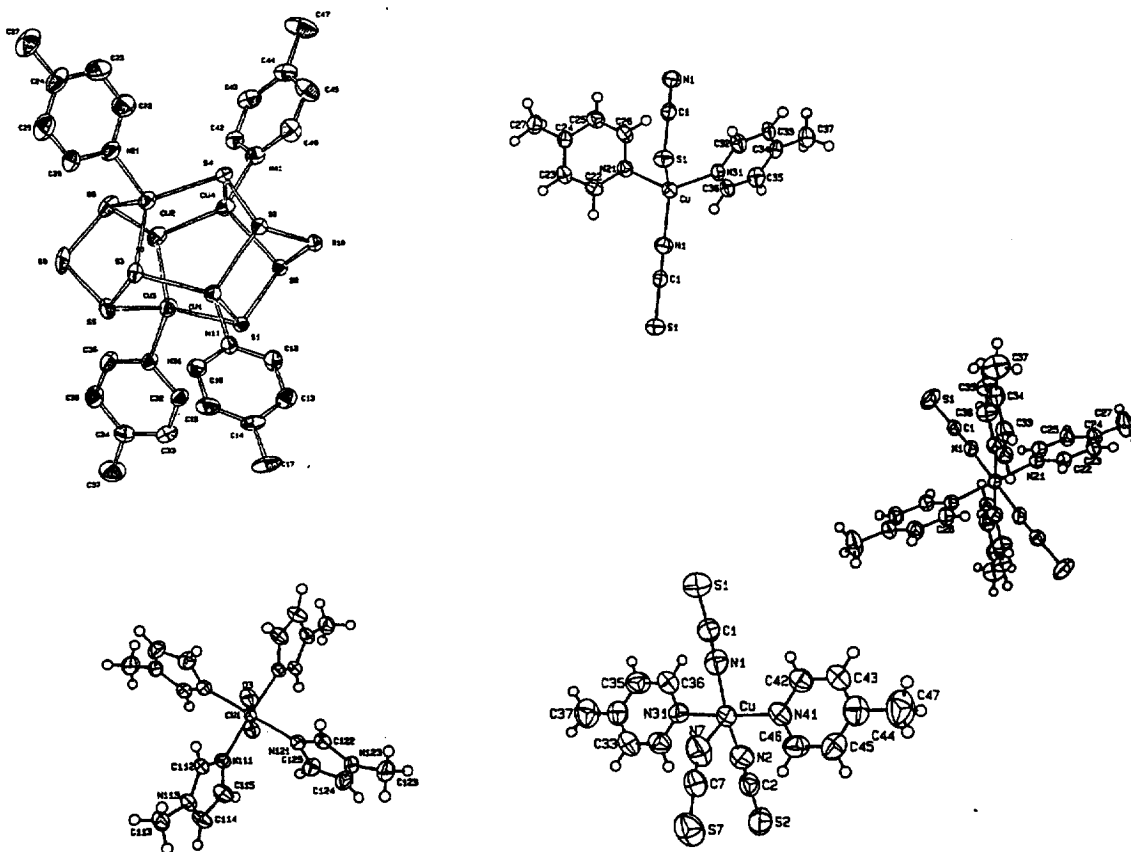


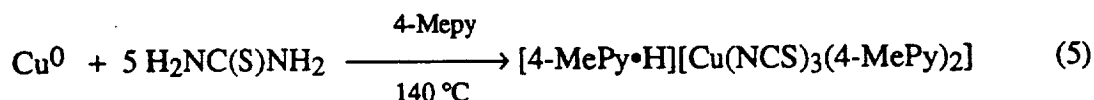
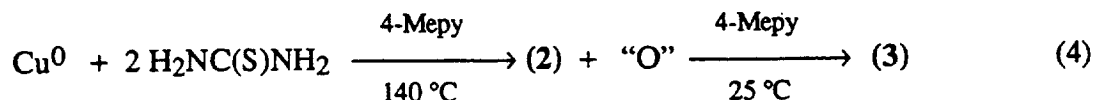
Figure 1. - ORTEP drawings of compounds (1) - (5). The thermal ellipsoids enclose 50 % of electron density. Compounds are shown clockwise with (1) in upper left-hand corner.

TABLE 1. X-RAY DATA SUMMARY FOR COPPER COMPOUNDS

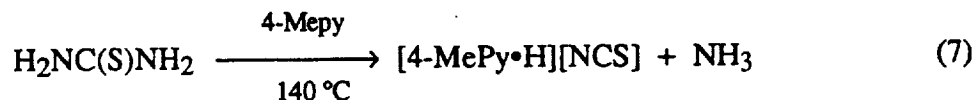
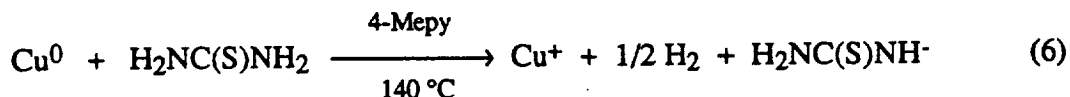
Compound	(1)	(2)	(3)	(4)	(5)
<i>a</i> , Å	13.983 (2)	8.4138 (8)	14.656 (1)	16.070 (1)	9.0754 (6)
<i>b</i> , Å	15.384 (2)	5.8127 (7)	15.635 (2)		9.9729 (7)
<i>c</i> , Å	9.660 (1)	14.459 (2)	14.390 (1)	16.070 (1)	12.745 (2)
α	93.87 (1)°				98.342 (9)°
β	93.38 (1)°	106.783 (9)°	112.886 (7)°		95.367 (9)°
γ	99.78 (1)°				114.153 (5)°
<i>V</i> , Å ³	2037.9 (9)	677.0 (3)	3038.0 (1)	2381 (2)	1026.3 (4)
<i>Z</i>	2	2	4	3	2
form. weight	1040.42 g	307.88 g	611.31 g	620.31 g	488.02 g
space group	P1bar (#2)	P2 ₁ (#4)	Cc (#9)	R3 bar (#148)	P1bar (#2)
<i>T</i>	-120 °C	-70 °C	20 °C	-70 °C	20 °C
λ	0.71069	0.71073	0.71073	0.71073	0.71073
ρ_{calc} , g/cm ³	1.695	1.510	1.337	1.297	1.579
$\mu(\text{Mo K}\alpha)$	25.89 cm ⁻¹	17.49 cm ⁻¹	9.45 cm ⁻¹	8.29 cm ⁻¹	12.03 cm ⁻¹
<i>R</i> (<i>F</i> _o) ^a	0.026	0.028	0.043	0.071	0.031
<i>R</i> _w (<i>F</i> _o) ^b	0.036	0.037	0.053	0.090	0.038

^a $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $R_w(F_o) = [\sum w|F_o| - |F_c|]^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Other copper and sulfur containing compounds were obtained when thiourea ($\text{H}_2\text{NC(S)NH}_2$) instead of S_8 was reacted with copper metal. The reaction of copper powder with thiourea produced thiocyanate compounds, of which three were isolated and characterized. The three characterized products are: Cu(NCS)(4-MePy)_2 (2), $\text{t-Cu(NCS)}_2(4\text{-MePy})_4 \cdot (4\text{-MePy})_{2/3}(\text{H}_2\text{O})_{1/3}$ (3), and $[4\text{-MePy}\cdot\text{H}][\text{Cu(NCS)}_3(4\text{-MePy})_2]$ (4) figure 1. Compound (2) has been previously structurally characterized [23]. The formation of these compounds is a function of the ratio of thiourea to metal. Compounds (2) and (3) were isolated for a ratio of 2:1, (4), while (4) was isolated in a reaction with an 5:1 ratio, equation (5).

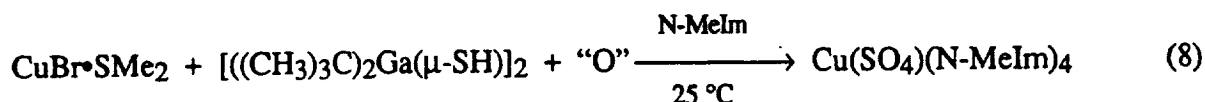


The first step in this reaction may be attack of thiourea of Cu^0 (6) to produce hydrogen where thiourea acts like an acid on copper. The $\text{H}_2\text{NC(S)NH}_2$ species can then rearrange to produce NCS^- and NH_3 . As discussed above, highly basic solvents promote the reaction of metals with sulfur. Another process that is likely is an acid/base reaction of thiourea with the solvent followed by rearrangement to produce NH_3 and NCS^- (7). The reaction does not occur at room temperature in 4-MePy or in boiling Py. The presence of both NCS^- and 4-MePy in the coordination sphere suggests a concerted reaction mechanism. A second oxidation step is indicated by the presence of two NCS^- ligands around the Cu(II) species, (3) and (4).



While (6) and (7) are reasonable proposed reactions, we have not as yet obtained direct evidence of hydrogen or NH_3 formation. Work is currently underway to observe these by-products. It should be noted that acidic solutions of thiourea are used to remove copper encrustations from boilers by dissolution of the copper materials. In this case the mechanism is acid solubilization of copper species with stabilization of Cu(I) species by thiourea [24]. Dry etching of Cu remains a challenge; solution systems offer a low-cost alternative.

Finally, an attempt to produce a mixed-metal sulfide precursor of Cu and Ga by reaction of $\text{CuBr}\cdot\text{SMe}_2$ and $[((\text{CH}_3)_3\text{C})_2\text{Ga}(\mu\text{-SH})]_2$ in N-methylimidazole (N-MeIm), reaction (8), resulted in the synthesis of a Cu-containing polymer, $\text{Cu(SO}_4\text{)(N-MeIm)}_4$ (5), figure 1 and table 1.



It is apparent that an oxidizing impurity led to the formation of the sulfate. Interestingly, this species has not been previously structurally characterized. We have previously observed similar chemistry. In an attempt to oxidize Cu powder with diphenyldisulfide in pyridine, the only isolable species that we characterized was $\text{Cu}(\text{C}_6\text{H}_5\text{SO}_3)_2(\text{Py})_4$ (6) [25]. The presence of the phenyl ring in (6) precludes polymerization and results in isolated molecules in the solid-state structure. Compound (5) can also be compared to an analogous compound $\text{Cu}(\text{SO}_4)(\text{Py})_4 \cdot \text{H}_2\text{O}$ that is polymeric but linked through hydrogen bonds through the sulfate groups [26]. A one-dimensional structure such as (5) may have relevance for molecular magnets [27]. There are recent reports of In/Cu chalcogenide precursor molecules that were used to produce CuInQ_2 (Q = S or Se), a material used in thin-film solar cells [13,14].

CONCLUSIONS

In the process of investigating reactions of copper and its compounds with sources of sulfur for aerospace applications, we have observed some interesting new chemistry and obtained structural characterization of a number of the compounds produced. The structure determinations found that the nature and degree of linkage of the copper atoms of these precursor materials varies. One of the compounds has a cluster structure while another has a copper coordination unit linked in a polymeric chain. In a third compound, the Cu atoms of neighbors are associated through a weak CuNCS-Cu interaction. The remaining two compounds described have discrete molecular units containing a single Cu atom. The varying chemistries that we observed when reacting copper and low-valent copper compounds with sources of sulfur show that these systems are very sensitive to reaction conditions and are driven to produce Cu(II) species. This experience will hasten the discovery of useful materials precursors and processing for applications.

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